

Study on Catalytic Ozone Oxidation with Nano-TiO₂ Modified Membrane for Treatment of Municipal Wastewater

Yueqi Zhu¹, Hongwei Zhang^{1,2*} and Xuehua Zhang^{1,2}

¹School of Environmental Science and Engineering, Tianjin University, 300072, China

²School of Economics, Tianjin Polytechnic University, 300160, China

Abstract

In this paper, we studied the application of Nano-TiO₂ Modified membrane technology in municipal wastewater treatment, which has not been previously reported to exhibit in this area. Ozone (O₃) aeration can produce a large number of high oxidizing free radicals (hydroxyl radical HO•) to degrade organic matters when ozone contacts with nano-TiO₂ Modified membrane, which process is called catalytic ozone oxidation process. This approach is a new frontier of municipal wastewater treatment, which has excellent reactive activity and degradation of organic compounds without the need of catalyst recycling. Our purpose is to remove organic matters by ozone aeration pre-treatment and nano-TiO₂ modified membrane. This method is more efficient since it combines both chemical oxidation and physical filtration. In this study, municipal sewage is called raw water. Polyvinylidene fluoride (PVDF) and the nano-TiO₂ modified PVDF ultra-filtration membranes are selected as experimental materials. Results suggest that the removal rate of organic matters with this new method (TiO₂+O₃) is 66.4%, which is 13.3% higher than original membrane with O₃ (PVDF+O₃) under the same condition. Therefore we can extract that, this part of contribution belongs to catalytic ozone oxidation process on TiO₂ modified membrane. Compared with traditional PVDF membrane filtration, whose removal rate is 38.7%, this novel approach has a removal rate 27.7% higher.

Keywords: Catalytic ozone oxidation; Modified ultra-filtration membrane; Nano-TiO₂; Treatment of municipal wastewater; Membrane fouling

Introduction

In recent decades, membrane separation technology as one of new high-efficiency separation techniques has developed rapidly. Compared with traditional separation techniques, membrane separation is highly efficient, energy-saving and easy to operate. Membrane separation technology has been widespread used and considered to be "one of the most promising high-techs from 20th century to the 21st century medium-term" [1].

In the past decades, plenty of reports indicated that ozone could be used as pretreatment of municipal wastewater treatment, because of its strong oxidizing property [2], but the process is expensive and hard to control [3]. Currently, several studies showed that the using of catalytic ozone oxidizing with metal oxides catalysts for organics degradation of waste, and it becomes a new trend of advanced oxidation technology [4].

Polyvinylidene Fluoride (PVDF) ultra-filtration membrane has good chemical stability and fiber durability, and it is widely used in membrane separation. Nano-TiO₂ modified membrane is a new membrane with Nano-TiO₂ coating on constituent particles of the PVDF membrane through micro-electrophoresis, which can catalyze ozone to produce a large number of high oxidizing free radicals (hydroxyl radical HO•) [5,6] to degrade organic matters inside/on the surface of membrane. In addition, the product of ozone oxidation is oxygen; accordingly catalytic ozone oxidation reaction is highly active without secondary pollution oxidants [7]. In a word, this experimental application of catalytic ozone oxidation in water treatment is mainly based on characteristics such as strong oxidizing property and non secondary pollution.

In this paper, the brand-new method of catalytic ozone oxidation with nano-TiO₂ modified PVDF membrane is used for treatment of municipal wastewater (raw water). This study put emphases on two aspects: 1. Analyze molecular weight distribution of organic matters in different water samples by molecular sieving membrane and compare

efforts of removal rate of catalytic ozone oxidation approach with traditional ones; 2. Study the mechanism of catalytic ozone oxidation by molecular weight distribution.

Ozone is a strong oxidant, research shows that ozone has strong oxidizing property and fast reaction ability, in the treatment of industrial wastewater, ozone oxidation is available for a variety of organic compounds. Why dose ozone have such a strong oxidizing property? Because the oxygen atom in the molecule has strong electrophilicity or protophilia and the nascent oxygen atom of the ozone decomposition also has high oxidation activity [8]. In aqueous solutions, ozone reacts with organic compounds in two ways [9]: ozone molecules direct attack and the free radical reactions by decomposition of ozone.

The stability of ozone is related pH, UV, ozone concentrations and the capture concentration of free radicals. The formation of free radicals depends on the ozone decomposition which causes free radical reactions [10].

Ozone decomposition reaction is carried out in a chain reaction, involving the following basic steps. Free radicals reaction is the rate-limiting step. In addition, the steps of producing ·O₂⁻ and ·HO₂ are also important, because these substances can increase the stability of ozone in the water. This machine includes a two-electron transfer process and one oxygen atom transfers from the ozone molecule to hydrogen peroxide ion.

*Corresponding author: Hongwei Zhang, School of Environmental Science and Engineering, Tianjin University, 300072, China, Tel: +86 13821653658; Fax: +86 022 23121662; E-mail: hunanzhilv@163.com

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Experimental Materials and Methods

Experimental materials

The raw water used in this study was obtained from a wastewater treatment plant in China. The water qualities are shown in Table 1.

The PVDF with nano-sized TiO₂ sol was prepared by sol-gel method. The structure and performance of the membrane were investigated by X-ray diffraction (XRD) scanning electron microscopy (SEM).

The synthesis method of the nano-TiO₂ modified PVDF membrane is as follows: add 10 mL dibutyl phthalate (DBP, A.R., Tianjin Fuchen Chemical Reagents Factory, China) into a certain amount of anhydrous ethanol (EtOH, A.R., Tianjin University Chemical Reagents Factory, China), and then drop dimethyl acetamide (DMAc, A.R., Tianjin Chemical Reagents Factory, China) containing nitric acid and distilled water into the solution under stirring, maintain this reaction for 24 hr at room temperature (25°C), thus gain transparent TiO₂ sol; with 0.10% of the mass fraction, put the sol into DMAc solution containing 7% polyvinylpyrrolidone (PVP, A.R., Tianjin Fuchen Chemical Reagents Factory, China) and 18% polyvinylidene fluoride (PVDF, A.R., Shanghai 3F New Material Co., Ltd., China), continuously stir for 24 hr, consequently get homogeneous hybrid casting solution; after static defoaming, pour the solution onto glass plate for knitting, after staying a while in the air, put it into the coagulating bath for film formation, as a result, the nano-TiO₂ modified PVDF membrane with average thickness d of 0.2 mm can be produced [11,12]. In this study, PVDF ultra-filtration membrane (Tianjin MOTIANMO Co., Ltd, China) and nanosized TiO₂ modified ultra-filtration membrane (0.10 w%) were used as experimental materials (Figure 1).

It can be seen from Figure 1 that nanosized TiO₂ modified ultra-filtration membrane has the advantage of high porosity. Compare Figure 1a with Figure 1b, because of the great adsorption process between PVDF and nanosized TiO₂, a large number of nanosized TiO₂ particles have been adsorbed and embedded in the membrane surface and in intra-pore. In the meanwhile, a significant increase in the profile layer can be observed as well as a decline in finger holes of sub-planes.

The white powder is nanosized TiO₂ by XRD (Figure 2), which can be found directly that even smaller particles are successfully prepared.

Parameters	Values
pH	8.04-8.35
Turbidity, NTU	11.39-18.61
DOC, mg/ L	95.27-106.31
COD _{Mn} ¹ , mg/ L	92.62-104.64
UV ₂₅₄ ¹ , cm ⁻¹	2.7-11.8

Table 1: Raw water quality parameters.

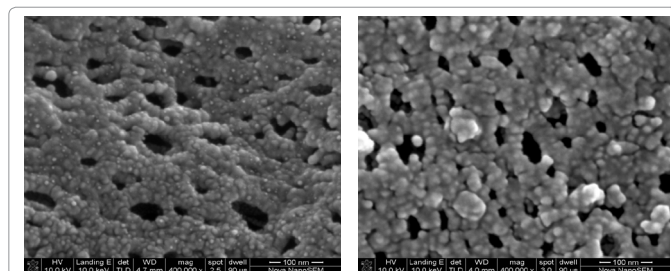


Figure 1: SEM micrograph of pure PVDF (a) and nanosized TiO₂ modified membrane surface view (b).

That means nanosized TiO₂ particles have content deposited regularity in the membrane surface and in intra-pore.

Experimental design

In the research, experimental devices are divided into three main groups, as shown in Figure 3 for membrane filtration, Figure 4 for ozone aeration pretreatment of raw water, and Figure 5 for molecular weight sieving respectively.

The experiment device in Figure 3 is used for raw water filtration and the water filtration after ozone aeration pretreatment.

Experimental device shown in Figure 4 is used for raw water ozone pretreatment. It can reach the target of ozone pretreatment to remove part organic matters. Meanwhile, extra ozone also can dissolve in the water and through the pipe. Catalytic ozone oxidation with nano-TiO₂ modified membrane will remove organic matters that stick to the membrane (physical trapping and catalytic ozone oxidation).

Device shown in Figure 5 is mainly used for molecular fractionation of raw water and percolates after different membranes (PVDF and nano-TiO₂ modified membranes). In the research, we use molecular sieve membranes of different apertures in order to trap organic matters of different molecular weights. In the end, molecular weight distributions are determined by COD_{Mn} [13].

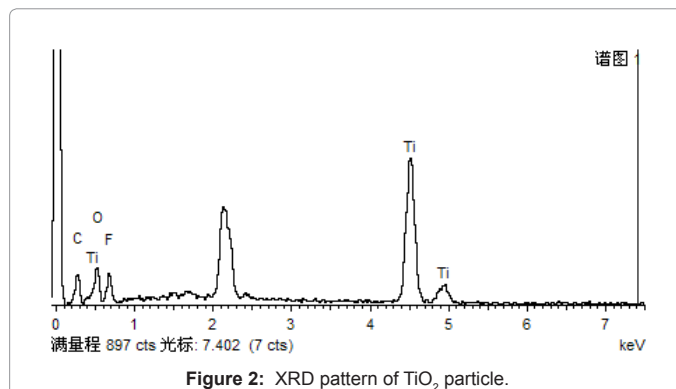
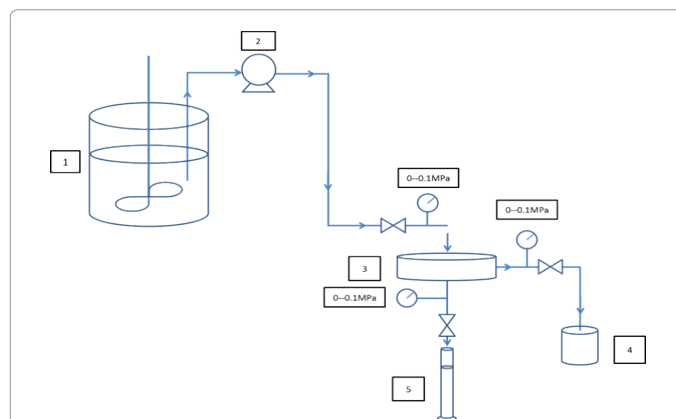


Figure 2: XRD pattern of TiO₂ particle.



1) Raw water/ water after ozone aeration pretreatment tank 2) Peristaltic pump 3) Membrane module 4) Water collection tank 5) Filtrated water tank.

Figure 3: Membrane filtration device - water sample flows from 1 to 3 by 2. There is a piece of membrane (PVDF/TiO₂ modified) in 3. The organic matters will be trapped and get into 4, and the filtrated water will be collected in 5.

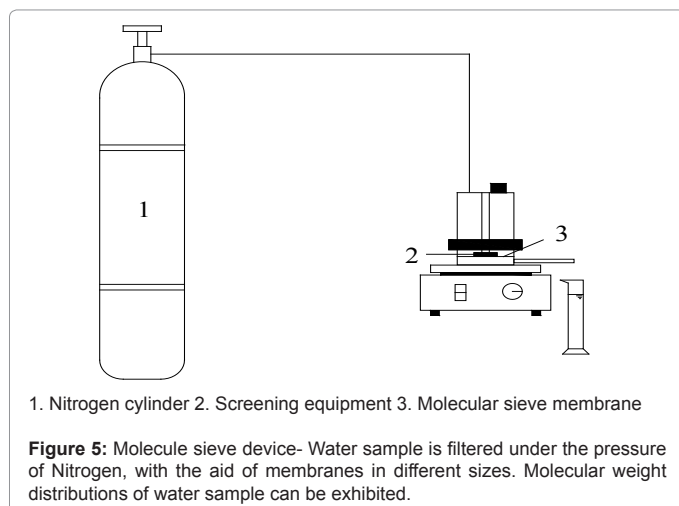
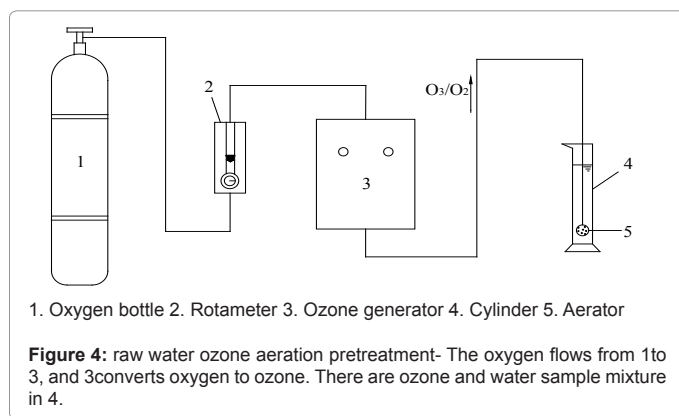
We sieve different molecular weight organics by plate Ultrafiltration membranes in different pore sizes as demonstrated in Table 2.

Analysis method of the molecular weight distribution of water

On the first stage, as shown in Figure 3, we filter raw water (water in wastewater treatment plant after primary treatment, meaning sinking sand and primary sedimentation) directly by PVDF membrane and TiO₂ modified membrane until the membrane is blocked up, and then trap percolates through molecular sieve membranes of 1 kDa, 3 kDa, 10 kDa, 30 kDa and 100 kDa apertures respectively. After that, we determine COD_{Mn} of percolates. On the second stage, as shown in Figure 4, under the operating condition of 1.34 mg/L ozone dosage and after aeration of 5 min, we make the samples go through PVDF and TiO₂ modified membranes. Then, repeat the first stage experiment after the ozone aeration pretreatment.

Identification of catalytic ozone oxidation function

In order to confirm the effect of catalytic ozone oxidation, we performed comparison experiment on PVDF+O₃ and (TiO₂+O₃) as shown in Figure 3 under the operating condition of 1.34 mg/L ozone dosage from 0 min to 10 min. The removal rate of COD_{Mn} is recorded every 2 min. Next, under the same condition, we added tertiary butyl alcohol (an inhibitor of HO•) to avoid the reaction of catalytic ozone oxidation. Catalytic ozone oxidation function can be verified from both comparison experiments.



Membrane size	Material	Range of molecular weight, Dalton
0.45μm	Cellulose Acetate	Diameter>0.45μm
100,000(100K)	Polysulfone	>100,000
30,000(30K)	Polysulfone	>30,000
10,000(10K)	Polysulfone	>10,000
3000(3K)	Polysulfone	>3000
1000(1K)	Polysulfone	>1000

Note: 1 Dalton (Da)=1.66×10⁻²⁷ kg.

Table 2: Material and molecular weight cut-off of the membrane.

Results and Discussion

Characterization of nano-TiO₂ modified membrane

It is found that if appropriate nano-sized TiO₂ sol is added the microstructure of PVDF membrane can be obviously improved. Meanwhile, the hydrophilic property and anti-fouling capability of the membrane can also be enhanced.

The surface views of PVDF and TiO₂ modified membranes after filtration are shown in Figure 6. In the filtration by PVDF membrane, the flux dropped rapidly due to membrane fouling in Figure 6a. It suggests that the membrane fouling occurred in the initial filtration. In the filtration by TiO₂ modified membrane, the flux kept well and there was no significant fouling in/on the membrane as shown in Figure 6b, also the flux recovered completely for each filtration cycle. We can conclude that organic matters inside/on the surface of membrane were degraded by high oxidizing free radicals (HO•).

The molecular weight distribution of organic matters

The molecular weight distribution of organic matters is shown in Figure 7.

According to Figure 7, in the raw water, the main organic matters are centered on >100k and 30k~100k scales, and COD of raw water is reduced by 2.5% with ozone aeration treatment. Therefore, we can infer that, after a short time, the ozone aeration does not reduce the COD significantly. As shown in Figure 7, the large organic matters reduces while the small ones get increased and the >100 kDa ones make the chief contribution to COD reduction. Meanwhile, the 3k~100k ones grow and others are not very obviously. That is mainly due to the strong selectivity of ozone reaction, this effort is only limited to unsaturated aromatic, aliphatic compounds and certain special groups. But ozone has little effect on low molecular weight organic acids such as acetic acid, and various types of compounds such as alkanes which almost have no response to ozone [14]. Thus, molecules of ozone play the main role in pre-treatment. This process is affected by ozone aeration time and concentration strongly.

After filtration of PVDF membrane, the reduction of COD in raw water is only 27.6%, but we can find the concentrations of macromolecular organic compounds (mainly in molecular weight between >100 kDa, 30 kDa~100 kDa organic compounds) reduce significantly. Therefore, traditional membrane filtering only has effect on large molecular weight organics. Also, after the soon followed membrane fouling, membrane pore is blocked. As a consequence PVDF membranes need to be cleaned or replaced frequently.

After ozone aeration pre-treatment, the removal of COD is obviously (above 50%). Organic compounds of molecular weight >100 kDa is reduced obviously (84.8%), the removal rate of smaller organic compounds (molecular weight 30 kDa~100 kDa) reaches 45.9%. Ozone makes macro-molecules organic compounds degrade into smaller ones.

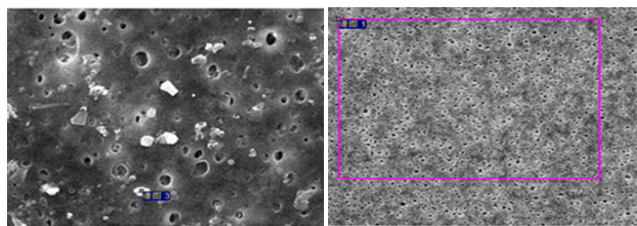


Figure 6: SEM micrograph of pore size of PVDF and TiO₂ modified membrane surface views after separation.

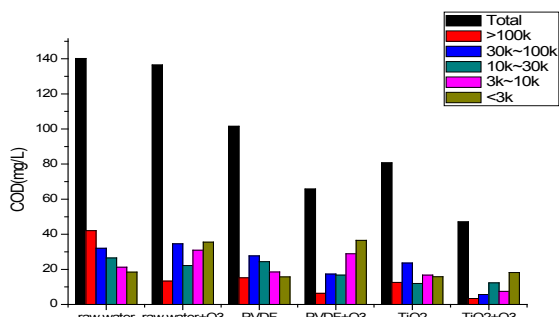


Figure 7: COD_{Mn} of different levels of treatment of water as a result of molecular sieve membranes.

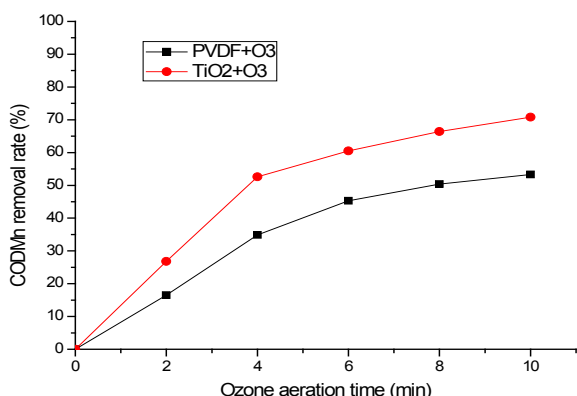


Figure 8: COD_{Mn} removal rates of PVDF+O₃ and TiO₂+O₃ as ozone aeration time increases.

That is why the organic compounds of >100 kDa removal rate rises significantly. Additionally, organic compounds of 30 kDa~100 kDa and 10 kDa~30 kDa can be removed by PVDF membrane mostly. Micro-molecules and macro-molecules degradation organic compounds (<10kDa) cannot be removed by PVDF membrane clearly.

After filtration of TiO₂ modified membrane, COD of raw water totally fell by 42.4%. TiO₂ modified membrane can almost remove organic matters of molecular weight above 10 kDa while has only a little effect on smaller ones (<10 kDa).

After ozone aeration pre-treatment and filtration of nano-TiO₂ modified membrane, we can gain the best removal result of organic matters -- total removal rate reaches 66.4%. Compared with PVDF+O₃, it rises by 13.3%. So we can extract that the contribution comes from catalytic ozone oxidation on TiO₂ modified membrane, for the reason that, after ozone aeration, there is still some ozone dissolved in the

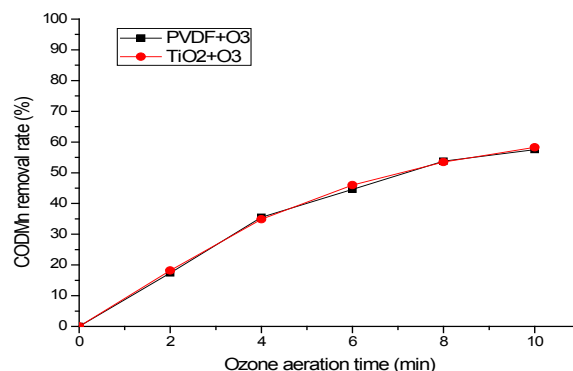


Figure 9: COD_{Mn} removal rates of PVDF+O₃ and TiO₂+O₃ with the addition of tertiary butyl alcohol.

water. When dissolved ozone goes through TiO₂ modified membrane, catalytic ozone oxidation helps to degrade organic matters. Compared with molecular ozone oxidation, ozone catalytic oxidation is speedy, full and non-selective. Therefore, this process (TiO₂+O₃) is to some extent better than others (Raw Water+O₃, PVDF, PVDF+O₃, TiO₂). There may be two processes existed in nano-TiO₂ catalytic ozone oxidation process: 1) Nano-Organics adsorbed on the surface. Adsorptive organic molecules, due to the changes in the electron cloud distribution, are easily to be oxidated. 2) Nano-TiO₂ catalytic ozone oxidation produces more HO·, which is useful to remove more organic matters than molecular ozone oxidation.

Figure 8 verifies the effect of catalytic ozone oxidation as follows: as the input of ozone aeration is increased, the removal rate of organic matters climbs up, which confirms that ozone can remove organic matters effectively. Meanwhile, process (TiO₂+O₃) is better than PVDF+O₃ under the same condition which means that catalytic ozone oxidation has contributed that part.

Catalytic ozone oxidation function

TiO₂ is good for the induction of ozone decomposition chain reaction and improve the generation of HO·. The reaction of HO· is non-selectively and the rate of the reaction is rapid, so the removal rate of TOC rises. If TiO₂ loaded in the hybrid membrane indeed catalyzes ozone and produces HO·, then the reaction will be seriously affected by tert-butyl alcohol, so we can indirectly judge whether the reaction follows the mechanism of HO· or not by examining the impact of tert-butyl alcohol.

As Figure 9 shows, with the addition of tertiary butyl alcohol (10 mg/L), there is not a clear difference in COD_{Mn} removal rates between PVDF+O₃ and TiO₂+O₃ approaches. Without free radical reaction of HO·, there is only reaction of molecular ozone in the water samples. This result proves the point that catalytic ozone oxidation process did take place and remove organic matters effectively.

As is showed in Figure 9, we can conclude that with the increasing of tert-butyl alcohol, the degradation of organics is strongly inhibited [15]. Compare Figure 9 with Figure 8, it is obviously that in the catalytic reactions of degradation of organics, HO· was dominant, and especially in the first six minutes, the inhibition capability of tert-butyl alcohol was obvious. Then the trend tended to become gentle because of the restriction of the concentration of catalyst.

According to Figure 9, due to the free radical reaction of HO· being inhibited by the addition of tert-butyl alcohol, there was no significant

difference between the two organic removal rates. With the increasing of ozone reaction time, the COD_{Mn} concentrations of water samples after filtrations of original membrane and TiO₂ modified membrane both dropped.

Conclusions

After ozone aeration pre-treatment and filtration of nano-TiO₂ modified membrane, we gain the best available removal effect of organic matters - total removal rate reaches 66.4%. Compared with PVDF+O₃, the total removal rate rises 13.3% under the same condition.

It is verified by comparison experiments that new method (TiO₂+O₃) can remove organic matters better than traditional membrane separation process. It is more efficient, combining catalytic ozone oxidation, ozone oxidation and physical filtration.

In order to verify the function of catalyzed ozonation, tert-butyl alcohol is used as quenching reagent to detect operation and contribution of HO·. The result proved that catalyzed ozonation is efficient in removing most of organic pollutants followed the HO· oxidation process.

Consequently, catalytic ozone oxidation joint ozone aeration pre-treatment process can achieve better treatment effect than traditional process. Compared with traditional process (PVDF membrane filtration) whose removal rate is 38.7%, this novel approach is 27.7% higher. Meanwhile, ozone catalytic oxidation removes the organic matters sticking to the membrane, which is an effective way to prevent membrane fouling.

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